

DEVELOPMENT OF THIN FILM HYDROUS METAL OXIDE SUPPORTED CATALYSTS FOR DIRECT COAL LIQUEFACTION*

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INTRODUCTION

In order to achieve optimum yields of distillate, current two-stage liquefaction processes, as evaluated in pilot research facilities consume as much 4 to 8 lbs of catalyst per ton of moisture-free coal fed to the reactors. The cost of catalyst for these replacement rates ranges from \$4 to \$6 per barrel of distillate product. If the cost of disposal of spent catalyst is considered, the cost could be substantially more. Thus a very important factor in achieving \$30/bbl liquids from coal is the development of less expensive catalysts or catalysts with better activity, selectivity and life.

The goal of this project is to develop catalysts, based on hydrous metal oxide (HMO) ion exchangers, that improve the efficiency and economics of conversion of coal to distillate products. Continuous reactor tests performed by AMOCO [1,2] have shown that preliminary formulations of one member of this class of catalysts, NiMo hydrous titanium oxide (HTO) catalysts were comparable or superior to 25 other commercial and novel formulations tested by AMOCO for second-stage upgrading of coal-derived resid. Thus efforts have focused on optimizing HTO supported catalysts, and recent research has resulted in formulation of NiMo/HTO catalysts with lower active metal loadings and increased activity. This paper reports the status of recent HTO catalyst research, especially the development of thin-film HTO-coated supports.

Although other HMOs, based on Zr, Nb or Ta may also provide good catalyst supports, HTO supports were chosen for initial development because the raw materials required to form HTOs are more readily available and less expensive than those required for other HMOs. A promising method to produce inexpensive catalysts with properties tailored to a specific process is the application of HTO catalysts as thin film coatings on other support structures. Development effort has concentrated on molybdenum as the major active metal in both the bulk and thin-film HTO catalysts. The choice of molybdenum as the major active component is based

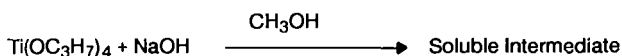
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on the fact that the most successful liquefaction catalysts currently in use (e.g. Shell 324M and Amocat 1C) contain molybdenum as the major active metal. Catalysts developed in this program have been evaluated with laboratory micro-scale reactors, and will ultimately be evaluated with bench-scale units, such as the PETC Generic Unit, and a large-scale process development unit.

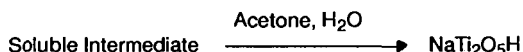
CATALYST PREPARATION

Hydrous titanium oxide catalysts are prepared by a technique that consists of synthesis of sodium hydrous titanate ion exchange material followed by ion exchange of the sodium for active metal ions [3]. The synthesis involves three steps:

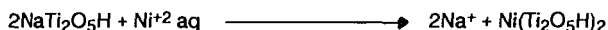
- (1) Reaction of tetraisopropyl titanate with sodium hydroxide in alcohol solution to form a soluble intermediate:



- (2) Hydrolysis of the soluble intermediate in acetone/water mixtures to form the hydrous metal oxide ion exchange material:



- (3) Ion exchange of the sodium for active metal ions in aqueous solution to form the catalyst:



In addition to the capacity to exchange metal cations, contact of the ion-exchangers with acidic solutions results in exchange of hydrogen ions, which alters the acidity and catalytic activity of the material. The materials can also function as anion exchangers in acidic solutions, allowing adsorption of metals that exist as aqueous oxygenated anions; molybdates, for example.

Catalyst preparation by coating inert supports with a thin film of a hydrous metal oxide ion-exchanger offers the potential of tailoring catalyst activity and selectivity by appropriate choice of active metal combinations and substrate physical properties such as strength, surface area, and pore size. Additionally, an excellent dispersion of active metals may be achieved by this technique.

Preparation of coated-support catalysts involves three steps:

- (1) Synthesis of the water or alcohol soluble hydrous titanium oxide as in step (1) above;

- (2) Deposition of an ion exchange coating by contacting the support with an aqueous or alcoholic solution of the soluble hydrous titanium oxide ion exchanger;
- (3) Ion exchange of the cations of the HTO coating for those of a catalytically active metal in aqueous solution as in step (3) above.

Because active metals are dispersed on HTO catalysts by ion exchange, they are chemically associated with the HTO support. Therefore activation techniques must result in release of the active metal components from the HTO support. For example, activation [4] of Mo-based HTO catalysts is performed in two steps: (1) calcination in air at 500°C to release the Mo and promoter ions from the HTO structure, followed by (2) sulfidation at 425°C with a 10% mixture of H₂S in H₂.

CATALYST TESTING

Initial tests have been conducted on powdered (-100 mesh) and particulate catalysts (granular, extrudate, or spherical) using batch microautoclaves for rapid screening of a large number of preparations to determine their activity for model reactions such as pyrene hydrogenation and dibenzothiophene desulfurization. The batch microautoclaves have liquid reactant capacities of 2 cc and a gas-phase volume of 25 cc. Four reactors can be operated simultaneously. A typical experiment is carried out as follows. After being charged with the catalyst and reactant, the reactors are heated to temperature in a fluidized sand bath while being shaken with a wrist-action motion at 200 cycles/min. Temperatures and pressures are recorded with a digital data acquisition system during the course of the experiments. Following the heating period, the reactors are rapidly quenched to ambient temperature, a gas sample is taken and the products are removed for analysis by various techniques, including gas and liquid chromatography and elemental composition. For sulfided NiMo catalysts, pyrene hydrogenation tests are typically carried out at 300°C and 500 psig cold charge hydrogen pressure, and dibenzothiophene desulfurization at 350°C and 1200 psig. For the more active noble metal catalysts such as Pd/HTO, pyrene hydrogenation experiments are typically performed at 100°C and 100 psig.

RESULTS AND DISCUSSION

Bulk-Phase NiMo/HTO Catalysts

The development of NiMo/HTO catalysts has progressed to the point where the hydrogenation activity of HTO-supported materials, as measured by the hydrogenation of pyrene, is significantly higher than that of commercially available NiMo/Al₂O₃ catalysts used for coal liquefaction. NiMo/HTO catalysts exhibiting pseudo-first-order rate constants for pyrene hydrogenation of 0.19 sec⁻¹ g cat⁻¹ (1.66 sec⁻¹ g Mo⁻¹) for the powdered catalyst (-100 mesh) can be routinely prepared.

This hydrogenation activity can be compared to that of $0.16 \text{ sec}^{-1} \text{ g cat}^{-1}$ ($1.21 \text{ sec}^{-1} \text{ g Mo}^{-1}$) for powdered Shell 324M in tests run under identical conditions.

Further advances in catalytic activity have been made via a combination of HTO substrate modification and changes in metal loading techniques. Addition of tetraethylorthosilicate in the first step of the synthesis to achieve a Ti/Si ratio of 0.2 for the ion-exchanger was found to further increase activity. The $\text{Na}_{0.5}\text{Ti}/0.2\text{Si}$ supports were converted to the $\text{H}_{0.5}\text{Ti}/0.2\text{Si}$ form prior to metal loading. Mo was introduced onto the support via an ion exchange reaction. Following drying at 100°C , Ni was introduced by wetting with a minimum amount of aqueous $\text{Ni}(\text{NO}_3)_2$ solution. With this method, most, but probably not all of the Ni is fixed on the support via ion exchange. After the Ni loading step, the materials were dried at 100°C , pelletized, calcined at 500°C , and sulfided at 425°C prior to testing. The powdered form of this catalyst (8.69% Mo, 2.95%Ni) was found to have a pseudo-first-order rate constant for pyrene hydrogenation of $0.22 \text{ sec}^{-1} \text{ g cat}^{-1}$ ($2.32 \text{ sec}^{-1} \text{ g Mo}^{-1}$). The catalyst weight basis desulfurization activity as measured by the pseudo-first-order rate constant for dibenzothiophene desulfurization ($0.027 \text{ sec}^{-1} \text{ g cat}^{-1}$) was found to be the same as that for freshly sulfided, -200 mesh Shell 324M (0.027). However, on a weight of Mo basis, the desulfurization activity is about 50% greater, because of the lower Mo loading on the Si modified HTO catalyst. It appears that the increase in activity due to silicon addition is achieved, in part, by the stabilizing effect that Si has on the surface area of the calcined and sulfided catalysts. Catalysts containing silicon have approximately 60% higher surface area than preparations without silicon (150 vs $90 \text{ m}^2/\text{g}$).

Transmission electron microscopy (TEM) of the sulfided NiMo/HTO and commercial NiMo/alumina catalysts has shown that the greater activity of the HTO catalysts appears to result from a better dispersion of the Mo sulfide crystallites. Whereas the alumina catalysts appear to contain 50 to 70 angstrom-size stacks of 4-6 MoS_2 layers supported on amorphous alumina (figure 1), the HTO catalysts contain 50 to 70 angstrom-size crystallites of only 1-2 MoS_2 layers supported on 100 to 150 angstrom diameter anatase crystallites (figure 2) formed during the calcination process.

HTO-Coated Catalyst Supports

The information obtained from the development of bulk-phase HTO catalysts was found to be directly applicable to the preparation of thin-film NiMo/HTO catalysts on pre-formed supports. Application of HTO catalysts as thin films on support material is a promising approach to preparing inexpensive catalysts, because smaller amounts of HTO ion-exchanger material and active metals are required, and inexpensive supports may be used. Initially thin-film NiMo/HTO catalysts supported on a material referred to as controlled pore glass (CPG), available in -20 mesh granular form, were prepared. Results of experiments performed to compare the hydrogenation activities of bulk-phase and thin-film Pd/HTO-coated and NiMo/HTO-coated CPG catalysts showed that the thin-film catalysts had comparable or greater activities on a weight of active metal basis.

Recently NiMo/HTO-coated catalysts have been prepared using a porous silica support in spherical form, 1.5 mm in diameter. The silica spherical support has a surface area of 55 m²/g, an average pore diameter of 77 nm, and a total pore volume of 1.00 cc/g. The spheres were first coated with a thin film of HTO followed by exchange of Mo and Ni onto the thin film to achieve nominal Mo loadings of 1% and Ni loadings of 0.3%. Following calcination and sulfidation, the catalysts were tested for their activity for hydrogenation of pyrene to 4,5-dihdropyrene at 300°C, and desulfurization of dibenzothiophene at 350°C. These spherical silica NiMo/HTO-coated catalysts had weight basis rate constants for pyrene hydrogenation of 0.032 ± 0.003 sec⁻¹-g cat⁻¹ as compared to 0.041 for Shell 324M extrudate (0.78 mm diameter by 4 mm long) and 0.038 for Amocat 1C extrudate (1.59 mm diameter by 6 mm long). On a weight of active metal (Mo) basis, the rate constants ranged from 2.6 to 3.5 sec⁻¹ g Mo⁻¹, a factor of ten greater than that of 0.31 for Shell 324M. For dibenzothiophene desulfurization, rate constants of 0.0081 ± 0.0003 sec⁻¹ g cat⁻¹ were determined for the NiMo/HTO-coated silica spheres, compared to 0.016 for Shell 324M. Thus the HTO-coated silica sphere catalysts, which contained only one-tenth as much active metal as Shell 324M, exhibited half of the dibenzothiophene desulfurization activity on a weight of catalyst basis. On a weight of Mo basis, because of the low active metal loadings, the HTO coated sphere catalysts had activities six times that of Shell 324M.

The high activity, on a weight of Mo basis, for these spherical silica HTO-coated catalysts is due, in part, to their high effectiveness factor (ratio of the rate constant for the catalyst spheres to that of the powdered catalyst), which was determined to be 0.75 (for hydrogenation), compared with the much smaller values of 0.27 and 0.22 for Shell 324M and Amocat 1C. This result is undoubtedly due, in part, to differences in the effective diffusivity resulting from the more open pore structures of the silica spheres. A factor contributing to the higher Mo weight basis activity of the NiMo/HTO-silica sphere catalysts is the better dispersion of MoS₂ achieved by the HTO coating process. TEM analysis (figures 3 and 4) has shown that, as with the case for the bulk-phase HTO catalysts, the MoS₂ crystallites for the coated catalysts consist of 50-70 angstrom-size crystallites of 1-2 layers of MoS₂ attached to small anatase crystallites. These results demonstrate that the HTO coating method can be used to produce a catalyst with a low active metal loading, satisfactory activity, and a geometry amenable to existing reactor systems.

CONCLUSIONS

Hydrous titanium oxides are extremely versatile materials for preparation of coal liquefaction catalysts. Screening tests of catalyst activity with feeds that model coal liquefaction reactions have shown that bulk HTO catalysts with activities significantly greater than commercial NiMo/alumina catalysts can be prepared. Preliminary formulations of bulk-phase NiMo/HTO catalysts have also performed well in continuous microreactor tests [1] for upgrading coal-derived resid. In addition, catalysts prepared from HTO-coated supports, containing one-tenth the active metals of commercial alumina-supported catalysts, have been found to exhibit high

hydrogenation and desulfurization activities on a weight of Mo basis. Thus, HTO-coated support materials offer a promising method to produce cost-effective catalysts with mechanical, physical and catalytic properties tailored to specific direct liquefaction process applications.

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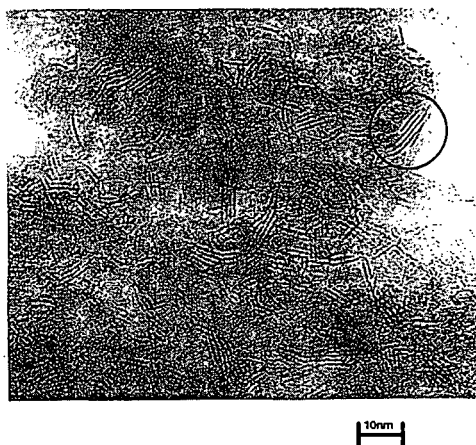


Figure 1. Transmission Electron Micrograph of sulfided NiMo/alumina catalyst containing 13.2% Mo and 2.7% Ni. A typical crystallite containing a "stack" of 4 MoS₂ layers (dark lines) is shown within circled area. Many other "stacks" of 4-6 MoS₂ layers can be observed.



Figure 2. Transmission Electron Micrograph of sulfided NiMo/HTO catalyst containing 10.2% Mo and 3.4% Ni. Typical crystallites containing one MoS₂ layer (dark line) conforming to the shape of an anatase crystallite is shown within circled area. Many other crystallites of one MoS₂ layer can be observed.

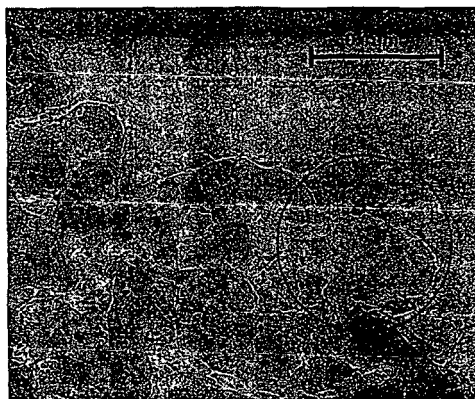


Figure 3. Transmission Electron Micrograph of sulfided NiMo/HTO supported on porous silica. This catalyst contains 1.3% Mo and 0.2% Ni. The silica support is seen as the larger irregularly shaped material (circled), approximately 100 nm in size. The smaller material (10 nm in size, darker spots) on the silica are crystallites of anatase with MoS₂ attached. The circled area is shown magnified by a factor of 3 in Figure 4.

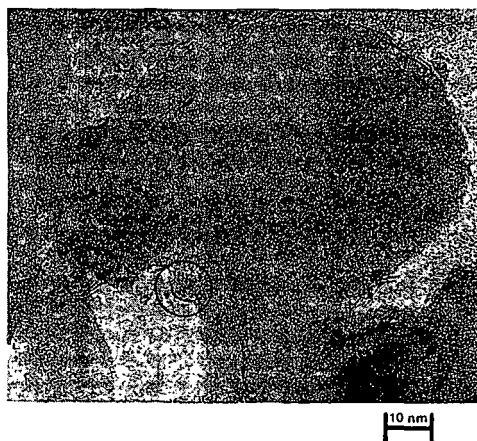


Figure 4. Transmission Electron Micrograph of sulfided NiMo/HTO supported on porous silica. The circled area shows a typical crystallite of anatase with a crystallite containing a single layer of MoS₂ (dark line) attached.